Esterification of maleic acid with ethanol over cation-exchange resin catalysts

G.D. Yadav*, M.B. Thathagar

Department of Chemical Engineering, University Institute of Chemical Technology (UICT) University of Mumbai, Matunga, Mumbai 400 019, India

Abstract

Diethyl maleate is an important intermediate extensively used in the production of latex emulsion polymers, thermoplast and thermoset plastics. The current paper delineates the efficacy of several heterogeneous catalysts, such as Indion-170, Amberlyst-36, Amberlyst-15, Amberlite IRA 120, 20% DTP/K-10 (dodecatungstophosphoric acid supported on K-10 clay) in the esterification of maleic acid with ethanol at reflux. Amongst these Indion-170, Amberlyst-36, Amberlyst-15 were observed to be the most effective. It was observed that the catalyst chosen has excellent reusability and was not deactivated. The effects of various parameters on the rate of reaction demonstrated that the reaction was intrinsically kinetically controlled and there were no intraparticle and interparticle mass transfer limitations. A pseudo-homogeneous kinetic model was developed from the experimental data and activation energy was found to be 14.2 kcal/mol, which also suggested that this reaction was intrinsically kinetically controlled.
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1. Introduction

Esterification is a very widely employed reaction in the organic process industry. Esters fall under a very wide category ranging from aliphatic to aromatic with various substitutions and multifunctional groups [1,2]. Organic esters are most frequently used as plasticisers, sol-vents, perfumery and flavor chemicals and also as precursors to a gamut of pharmaceuticals, agrochemicals and other fine chemicals.

Several synthetic routes have been used to make esters but most of them do not meet the stringent specifications that are being applied in the chemical industry and particularly in today's environmentally conscientious world. The most acceptable method of making an ester is to react the desired carboxylic acid with an alcohol, catalysed by mineral acids and the reaction is reversible [1,3]. Several methods are available to drive the reaction towards the product. One

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*Corresponding author. Present address (till August 2002): Johansen-Crosby Visiting Professor of Chemical Engineering, Michigan State University, East Lansing, MI 48824, USA. Tel.: +91-22-414-5616; fax: +91-22-410-5614.

E-mail address: gdy@udct.ernet.in (G.D. Yadav).

of them is to use an excess amount of alcohol and another is to remove the ester formed (or the co-product water) continuously. In the conventional industrial processes involving homogeneous acid catalysts, heterogeneous catalysts such as zeolites and other metal oxides, acid treated clays, cation-exchange resins, etc., are being exploited as the replacement due to their eco-friendly nature [4–7]. These catalysts are non-corrosive and easy to separate from the reaction mixture. They can also be used repeatedly over a prolonged period without any difficulty in handling and storing them. Apart from their prominence in separation and purification of products, ion-exchange resins have been used as catalysts in some important chemical manufacture such as methyl *tert*-butyl ether (MTBE), ethyl *tert*-butyl ether (ETBE), tert-amyl methyl ether (TAME), bisphenol-A, phenol alkylation and hydration of olefins.

Maleate esters such as dimethyl maleate (DMM), diethyl maleate (DEM) and dibutyl maleate (DBM) are extensively used in the production of latex emulsion polymers, thermoplast and thermoset plastics. These esters can be prepared by treating various alcohols such as methanol, ethanol, or butanol, respectively, with maleic anhydride in the liquid phase either with a monoester intermediate stage or by a direct route [4,8–11] or by using maleic acid. Esterification of maleic anhydride in presence of *p*-toluenesulphonic acid as a homogeneous catalyst to give diethyl maleate is reported [12]. Esterification of maleic anhydride with ethanol to produce diethyl maleate has been recently reported with high conversions by using a special type of ion-exchange resin. The product is then hydrogenated to give the linear alcohols which in turn are used as detergents. This process has been commercialized by Rohm and Haas with Kvaerner process technology and is successfully used by BASF in three large scale plants [13].

A lot of work has emanated on ion-exchange resins from the authors' institute and Sharma and co-workers have brought out the value of ion-exchange resins in a spectrum of industrially relevant reactions including state-of-the art reviews [14–16]. These papers have been supplemented recently by Harmer and Sun [13] who have discussed critically the post-1995 developments including industrial applications. Since the commercially available resins are thermally stable up to 120–150 °C, we have examined over past few years the efficacy of ion-exchange resins with reference to several other solid acids such as clays, zeolites, sulfated zirconia, clay supported heteropoly acids and metal halides, UDCaT-1 and UDCaT-2 for developing green industrial processes. These processes include esterifications [2,4,8,17–21], etherifications [6,22,23], acetalization [24], isomerisation [25], cyclization [26], alkylations [5,6,27–30], acylations [20,31–34] and other reactions [35]. In our laboratory, deactivation of ion-exchange resins has been studied and modeled for industrial alkylation [29,30] and acylation [34].

Several new ion-exchange resin catalysts have been designed and in particular, for esterification reactions, a surface functionalized resin has been developed to minimize byproduct formation such as ethers and olefins due to dehydration of the alcohol. Thus esters may be produced with a minimum formation of ether by-product by reacting an organic acid or ester with an alcohol at elevated temperatures in the presence of vinyl aromatic polymer beads which are surface functionalized with strongly acidic functional groups, the inner volume of the polymer beads remaining unfunctionalized [36].

The emphasis of the current work was to study in detail, the kinetics of esterification of maleic acid with ethanol over cheap and easily available catalysts, ion-exchange resins and clay supported heteropoly acids.

2. Experimental

2.1. Chemicals and catalysts

All chemicals and catalysts were procured from firms of repute and used without further

purification: Maleic acid (AR; s.d. Fine Chem, Mumbai, India), ethanol (Merck India), Filtrol-24 (Engelhard, USA), K-10 clay (Aldrich, USA), ion-exchange resins (IER) such as Indion-170 (Ion Exchange India, Mumbai, India), Amberlyst and Amberlite resins (Rohm and Hass, USA). 20% (w/w) Dodecatungstophosphoric acid (DTP)/K10 clay was prepared by a well-developed procedure in our laboratory [5,6].

2.2. Reaction procedure

The reaction was carried out in a 1×10^{-4} m^3 capacity glass reactor of 4.5×10^{-2} m I.D. equipped with four equally spaced full baffles and six-bladed turbine impeller. The reaction temperature was maintained by means of a thermostatic water bath in which the reaction assembly was immersed. Reactions were carried out by taking 0.05×10^{-3} kmol of maleic acid and 0.25×10^{-3} kmol of ethanol at a reflux temperature of 80 °C and 120 kg/m^3 catalyst loading. All catalysts were dried at 110 °C under vacuum for 4 h before use. The reaction mixture was allowed to reach the desired temperature and the initial/zero time sample was collected. Agitation was then commenced at sufficiently high speed measured with a tachometer. In most of the cases, alcohol was taken in far molar excess over maleic acid to drive the equilibrium away towards the ester formation.

2.3. Analysis and isolation of product

For kinetic measurements, samples were withdrawn periodically, filtered and analysed by chemical as well as instrumental methods. In chemical analysis, the reaction samples were titrated against alcoholic KOH solution, to determine the extent of reaction of the acid [13]. Gas chromatography (GC) analysis was also performed by using a 2 m $\times$ 3.2 mm I.D. S.S. column packed with 10% OV-17 on chromosorb WHP, by using a flame ionization detector and an integrator. The GC analysis was mainly done

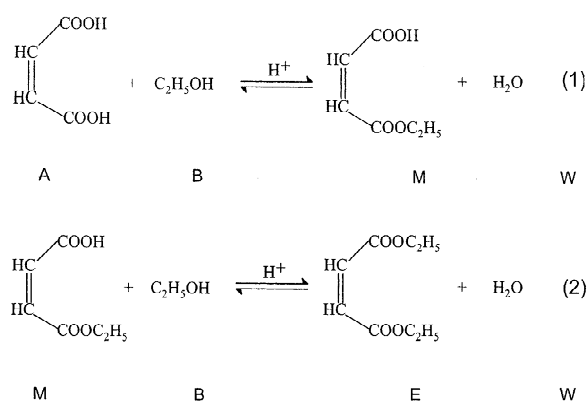to confirm the analysis. There was no byproduct formed.

For isolation of the product, the catalyst was filtered off and the excess unreacted ethanol was removed from the reaction mixture by using a rotovac. The remaining mass was treated with solid sodium carbonate to remove the unreacted maleic acid and then treated with diethyl ether to extract the ester in organic phase. The product was purified subsequently by vacuum distillation.

3. Results and discussion

The esterification of maleic acid involves two steps as shown in Scheme 1. The first reaction giving the monoester is very fast and in second stage the monoester formed reacts with another mole of ethanol to give diethyl maleate in presence of catalyst. As stated earlier, to shift the equilibrium towards the formation of the desired product, excess ethanol was used in the reaction. The preliminary experiments were conducted under otherwise similar conditions of reactant concentration (or mole ratio), catalyst loading, particle size, speed of agitation, and temperature except the type of catalyst.

3.1. Efficacies of various catalysts

Different solid acid catalysts were used to assess their efficacy in this reaction as men-

Scheme 1. Esterification of maleic acid with ethanol.

tioned earlier. A 120 kg/m³ loading of catalyst, based on the organic volume of the reaction mixture was employed at a mole ratio of maleic acid to ethanol (95%) of 1:5 at 80 °C and 13.33 rps. It was expected to have no influence of external and/or internal resistance to mass transfer so that a comparative study based on intrinsic kinetics could be made. Fig. 1 shows the plots of the conversion of maleic acid, the
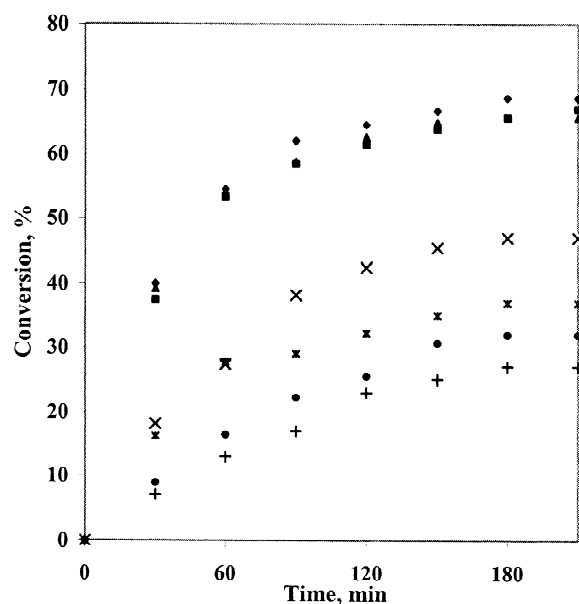
limiting reactant, against time for various catalysts.

It was found that the use of cation-exchange resins such as Amberlyst-36, Amberlyst-15 and Indion-170 resulted in higher conversions compared to other catalysts. The activities are in order of cation-exchange capacity on dry basis for Amberlyst-36, Indion-170, Amberlyst-15 and Amberlite IRA 120 are >5.40, 4.8, 4.8 and 1.9 mequiv./g, respectively, whereas for clays these values are less than 0.5 mequiv./g. The presence of water has a detrimental effect of activity of clay based catalysts. The properties of the resins are given in Table 1. 20% DTP/K10 has been found to be a better catalyst than K10 montmorillonite clay for several alkylation reactions [5,6,25–28] and so it was better than K10 for esterification. Since there was no significant difference in the final conversions (Fig. 1), further experiments were conducted with Indion-170 as the catalyst, where only one parameter was varied at a time under otherwise similar experimental conditions. The choice of Indion-170 was also based on its availability in the local market at much cheaper rates than the imported Amberlyst-31.

Fig. 1. Effect of different catalysts. Catalyst loading = 120 kg/m³, temperature = 80 °C, speed of agitation = 13.33 revolutions per sec (rps), ethanol to maleic acid mole ratio = 5:1. ♦, Amberlyst-36; ▲, Indion-170; ■, Amberlyst-15; ×, Amberlyst-18; * Amberlite IRA 400; ● 20% (w/w) DTP/K-10; + Filtrol-24.

3.2. Effect of speed of agitation

The effect of speed of agitation was studied in the range of 8.33–16.67 rps at a catalyst loading of 120 kg/m³ (Fig. 2). It was found that

Table 1
Properties of cation exchanged resins

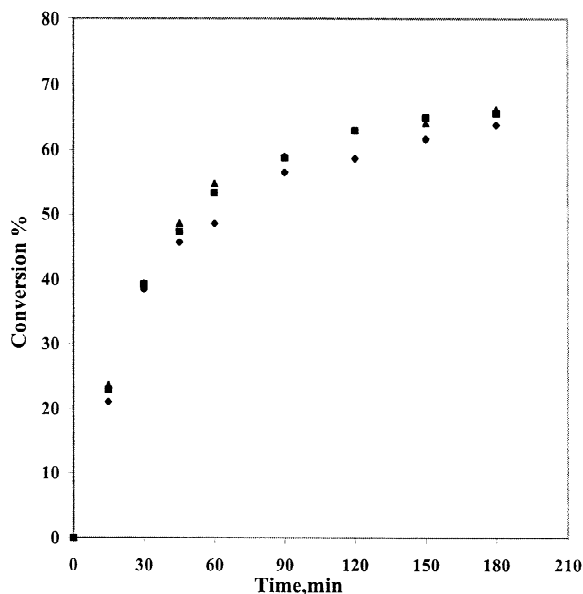|	Amberlyst-36	Amberlyst-15	Amberlyst-18	Amberlite IR-120	Indion-170
Manufacturer	Rohm and Haas	Rohm and Haas	Rohm and Haas	Rohm and Haas	Ion Exchange India
Polymer type	MR (macroreticular)	MR	MR	Gel—strongly acidic	Gel—strongly acidic
Matrix type	SAC	SAC		Styrene–divinylbenzene (DVB)	Styrene–DVB
Functional group	$-SO_3^-H^+$	$-SO_3^-H^+$	$-SO_3^-H^+$	$-SO_3^-H^+$	$-SO_3^-H^+$
Standard ionic form	H^+	H^+	H^+	H^+	H^+
Particle size range (mm)	0.45	0.50	0.50	0.45–0.60	0.35–1.2
% Moisture	55	Dry	Dry	50	63–66
Maximum operating temperature (°C)	150	120	120	120	120
Total exchange capacity (mequiv./g)	5.40	4.70	4.7	1.9	4.8

Fig. 2. Effect of speed of agitation. Catalyst loading = 120 kg/m^3, temperature = 80 °C, ethanol to maleic acid mole ratio = 5:1. ♦, 8.33 rps; ■, 13.33 rps; ▲, 16.67 rps.

there was practically no change in the conversion beyond 13.33 rps. Therefore, further experiments were conducted at 13.33 rps. A theoretical analysis was also done.

3.2.1. Theoretical aspects of solid catalysed liquid-phase esterification reaction

The solid acid catalysed esterification is a typical solid–liquid slurry reaction for which some theoretical work has emanated from this laboratory [37]. The theory takes into account the evaluation of the intrinsic kinetics of the reaction.

The esterification reaction involves two organic phase reactants, A (maleic acid) and B (alkanol); and the desired product E (dialkyl maleate) and W (co-product water) as shown in Scheme 1.

At steady state the rate of mass transfer per unit volume of the liquid phase can be given by:

$$R_A \text{ (kmol/m}^3 \text{ s)} = k_{\text{SL-A}} a_p \{[A_0] - [A_S]\} \qquad (3)$$

(the rate of transfer of A from bulk liquid phase to the catalyst surface)

$$R_A \text{ (kmol/m}^3 \text{ s)} = k_{\text{SL-B}} a_p \{[B_0] - [B_S]\} \qquad (4)$$

(the rate of transfer of B from bulk liquid phase to the catalyst surface)

$$= r_{\text{obs}} \qquad (5)$$

(the observed rate of reaction).

All these rates are based on unit volume of the liquid phase.

The observed rate of reaction r_{obs} can be given by different models. When the adsorption and/or the desorption steps are likely to be important, Eq. (5), can be replaced by the Langmuir–Hinshelwood–Hougen–Watson type of model invoking adsorption constants and fractional coverage of sites by the reactants. Otherwise it can be a power law model. In the presence of intraparticle diffusion limitation, the effectiveness factor η comes in to the picture.

When the surface reaction is very rapid with respect to the diffusion of A and B or of either A or B alone, several interesting cases emerge depending on the concentration of A and B in the liquid phase. When the external mass resistance is negligible the following inequality holds:

$$\frac{1}{r_{\text{obs}}} \gg \frac{1}{k_{\text{SL-A}} a_p [A_0]} \quad \text{and} \quad \frac{1}{k_{\text{SL-B}} a_p [B_0]} \qquad (6)$$

then either the surface reaction is the controlling mechanism or intraparticle diffusion resistance will control the overall rate of the reaction.

The influence of intraparticle diffusion, reflected in the effectiveness factor η can be studied by varying the particle size and also through the reaction temperature.

Since alcohol [B] was chosen in far excess, there is a possibility of diffusional resistance for transfer of maleic acid [A] through the liquid film around the catalyst and then inside the pores. According to the model used for this analysis, the liquid phase diffusivity values D_{AB} (maleic acid in ethanol) and D_{BA} (ethanol in maleic acid) were required and these values were calculated by using the Wilke–Chang equation [38], as 1.634×10^{-9} and 2.644×10^{-9}

m^2/s, respectively. The effective diffusivity $D_{e\text{-}A}$ was calculated to be 1.634×10^{-10} m^2/s from $D_{e\text{-}A} = D_{AB}\varepsilon/\tau$ where values of ε and τ were taken as 0.3 and 3, respectively.

The values of solid–liquid mass transfer coefficients $k_{SL\text{-}A}$ and $k_{SL\text{-}B}$, were calculated by using the correlations of Sano et al. [39] which has been developed for ion-exchange type catalyst and it takes into account the effects of Reynolds and Schmidt numbers:

$$\frac{k_{SL} d_p}{D_e \psi} = 2 + 0.4 \left(\frac{e d_p^4 \rho_L^3}{\mu_L^3} \right)^{1/4} \left(\frac{\mu_L}{\rho_L D_e} \right)^{1/3} \quad (9)$$

where:

$$e = \frac{P}{\rho_L V_L}$$

= energy supplied per unit mass of slurry

     by agitation, m^2/s^3 (10)

$$P = N_p N^3 D_I^5 \rho_L, \text{ power supplied/volume} \quad (11)$$

Thus, $k_{SL\text{-}A}$ and $k_{SL\text{-}B}$ were calculated as 4.345×10^{-5} and 5.761×10^{-5} m/s, respectively, for a particle size of Indion-170 of 425 μm. The value of a_p, particle surface area per unit liquid volume was calculated by assuming a spherical particle:

$$a_p = \frac{6w}{(\rho_p d_p)} \text{ as } 11.29 \times 10^2 \text{ m}^{-1} \quad (12)$$

For a typical experiment, the rates of mass transfer are calculated as:

$$k_{SL\text{-}A} a_p [A_0] = 1.376 \times 10^{-1} \text{ kmol m}^{-3}\text{ s}^{-1} \quad (13)$$

and:

$$k_{SL\text{-}B} a_p [B_0] = 8.956 \times 10^{-2} \text{ kmol m}^{-3}\text{ s}^{-1} \quad (14)$$

The typical initial rate of reaction was calculated as 1.76×10^{-4} $kmol/m^3$ s.

Therefore, after substituting all the calculated values in Eq. (6):

$5.681 \times 10^3 \gg 7.27$ and 11.622 $(m^3 \text{ s/kmol})$

$$(15)$$

The above inequality demonstrates that there is an absence of resistance due the solid–liquid external mass transfer and the rate may be either surface reaction controlled or intraparticle diffusion controlled, for which the following studies were conducted.

3.3. Effect of particle size

The effect of particle size on conversion was studied for three different particle size ranges (Fig. 3). For an average particle size less than 400 μm., there was no effect of particle size on the conversion of maleic acid, which would suggest that the effectiveness factor for this reaction is almost unity and the entire process was surface reaction controlled. This was further confirmed by invoking the Wiesz–Prater criterion [40].

According to the Wiesz–Prater criterion, the dimensionless parameter C_{WP} which represents
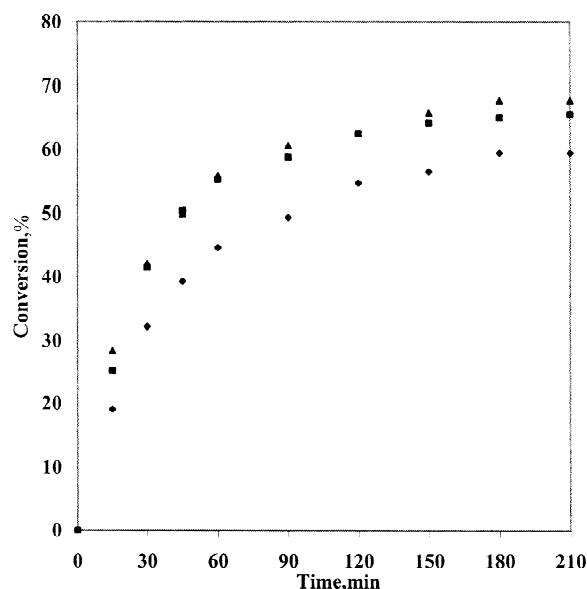

Fig. 3. Effect of particle size. Catalyst loading = 120 kg/m^3, temperature = 80 °C, speed of agitation = 13.33 rps, mole ratio of ethanol to maleic acid = 5:1. ♦, 500–600 μm; ■, 400–450 μm; ▲, 300–350 μm.

the ratio of the intrinsic reaction rate to intra-particle diffusion rate, can be evaluated from the observed rate of reaction, the particle radius (R_p), effective diffusivity of the limiting reactant (D_e) and concentration of the reactant at the external surface of the particle:

(i) If $C_{WP} = r_{obs} \rho_p R_p^2 / D_e [A_s] \gg 1$, then the reaction is limited by severe internal diffusional resistance.
(ii) If $C_{WP} \gg 1$, then the reaction is intrinsically kinetically controlled.

In the present case, the value of C_{WP} was calculated as 0.00595, which is much less than 1. Therefore the reaction was intrinsically kinetically controlled. A further proof of the absence of the intra-particle diffusion resistance was obtained through the study of the effect of temperature.

3.4. Reaction kinetics

Since the external mass transfer resistance and the intraparticle diffusional resistance were absent, the reaction was kinetically controlled. A power law kinetic model was used in order to validate the experimental data. The catalyst used is a macroporous ion-exchange resin. This is because, in a macroporous resin, the pores are so large (>400 Å) that the reactants are able to diffuse into the pores and the products to diffuse out without any resistance. This is the so called pseudo homogeneous model [39].

3.4.1. Kinetic model

The reaction proceeds in two consecutive steps as shown below by Eqs. (16) and (17):

$$A + B \overset{H^+}{\rightleftharpoons} M + W \tag{16}$$

$$M + B \overset{H^+}{\rightleftharpoons} E + W \tag{17}$$

The first of the two steps is assumed to be much faster as compared to the second step. Hence, at any instant, the monoester can be

considered to be in equilibrium with the maleic acid and ethanol.

Therefore, by steady state approximation the concentration of monoester is:

$$C_M = K' \cdot \frac{C_A C_B}{C_W} \tag{18}$$

The concentrations are related to the fractional conversion of A:

$$C_A = C_{A0}(1 - X_A) \tag{19}$$

$$C_B = C_{A0}(M - 2X_A) \tag{20}$$

$$C_E = C_{A0} X_A \tag{21}$$

$$C_W = 2C_{A0} X_A \tag{22}$$

The rate of formation of diethyl maleate (E) can be represented as:

$$\frac{dC_E}{dt} = wk_1' C_M C_B - wk_2 C_E C_W \tag{23}$$

Substituting Eq. (18) in Eq. (23):

$$\frac{dC_E}{dt} = wk_1' K' \cdot \frac{C_M C_B^2}{C_W} - wk_2 C_E C_W \tag{24}$$

Let $k_1 = k_1' K' =$ forward reaction rate constant:

$$\frac{dC_E}{dt} = wk_1 \cdot \frac{C_M C_B^2}{C_W} - wk_2 C_E C_W \tag{25}$$

In terms of conversion X_A the equation can be written as:

$$C_{A0} \cdot \left(\frac{dX_A}{dt} \right)$$
$$= wk_1 C_{A0}^2 \left[\frac{C_{A0}(1 - X_A)(M - 2X_A)^2}{2C_{A0} X_A} - 2X_A^2 / K \right] \tag{26}$$

Since ethanol was taken in far excess, reverse reaction was not so dominant and hence the reaction was considered to be irreversible. Therefore the Eq. (26) becomes:

$$\left(\frac{dX_A}{dt}\right) = wk_1 C_{A0} \left[\frac{(1 - X_A)(M - 2X_A)^2}{2X_A} \right] \tag{27}$$

Thus, for M not equal to 1 the final equation after performing the integration on Eq. (27):

$$\frac{2}{(M-2)} \cdot \left[\frac{1}{(M-2)} \ln\left\{ \frac{M}{(M-2X_A)} \right\} - \frac{1}{(M-2)} \right.$$
$$\left. \times \ln(1 - X_A) - \frac{2X_A}{(M-2X_A)} \right] = wk_1 C_{A0} t = k't \tag{28}$$

3.5. Effect of catalyst loading

The catalyst loading was varied from 50 to 150 kg/m^3 based on the total volume of the reactants at a temperature of 80 °C (Fig. 4). It was found that with an increase in loading the conversion of maleic acid increased in consonance with the proportional increase in the active sites. In the absence of mass transfer

resistance the initial rate of reaction is directly proportional to the catalyst loading based on the entire liquid phase volume. This further supports that the controlling mechanism is the surface reaction on the pore wall. At higher catalyst loading the rate of mass transfer is excessively high and therefore there is no significant increase in the rate.

As shown by Eqs. (3) and (4), at steady state, the rate of external mass transfer (i.e., from the bulk phase in which A and B are located with concentrations $[A_0]$ and $[B_0]$ respectively) to the exterior surface of the catalyst is proportional to a_p, the exterior surface area of the catalyst where the concentrations of A and B are $[A_s]$ and $[B_s]$, respectively. For a spherical particle, a_p is also proportional to w, the catalyst loading per unit liquid volume. It is possible to calculate the values of $[A_s]$ and $[B_s]$. For instance:

$$k_{SL-A} a_p \{[A_0] - [A_S]\} = r_{obs} \text{ at steady state}$$
$$= 1.76 \times 10^{-4} \text{ kmol m}^{-3} \text{ s}^{-1} \tag{29}$$

Thus, putting the appropriate values, it is seen that $[A_0] \cong [A_s]$, similarly $[B_0] \cong [B_s]$. Thus, any further addition of catalyst is not going to be of any consequence for external mass transfer. The same data were once again used to plot left hand side (L.H.S.) of Eq. (28) vs. t to get a straight line passing through origin, the slope of which gave the value of k' (Fig. 5). k' values were plotted against catalyst loading, w, kg/m^3 and it was observed that with increase in w there was linear increase in k' (Fig. 6). Thus, it validates the model.

3.6. Effect of mole ratio of reactants

The concentration of ethanol had an influence on the reaction rate and on the conversion. Experiments were carried out by taking 5×10^{-5} kmol of maleic acid and the desired quantity of ethanol with a catalyst loading of 120 kg/m^3 at 80 °C. The mole ratios of MA:EtOH were 1:3, 1:5, 1:10, 1:15, (Fig. 7). As the mole ratio was
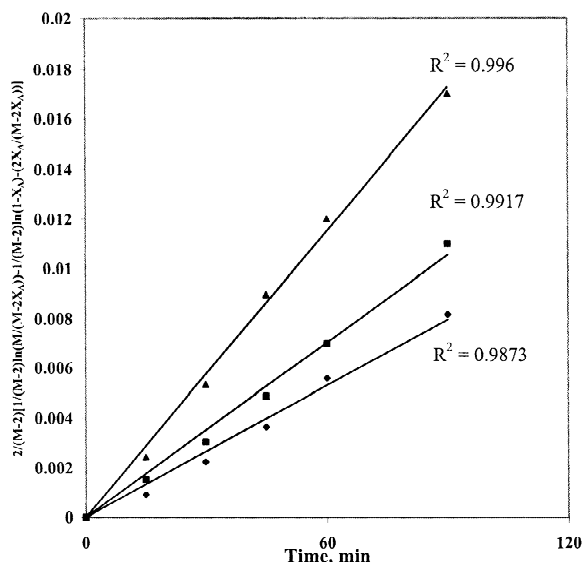

Fig. 4. Effect of catalyst loading. Speed of agitation = 13.33 rps, temperature = 80 °C, ethanol to maleic acid mole ratio = 5:1. ♦, 50 kg/m^3; ■, 80 kg/m^3; ▲, 120 kg/m^3; ●, 150 kg/m^3.

Fig. 5. Typical kinetic plot for the effect of catalyst loading. Particle size = 400–450 μm, temperature = 80 °C, speed of agitation = 800 rpm, mole ratio of ethanol to maleic acid = 5:1. ♦, 50 kg/m³ ■, 80 kg/m³; ▲, 120 kg/m³.
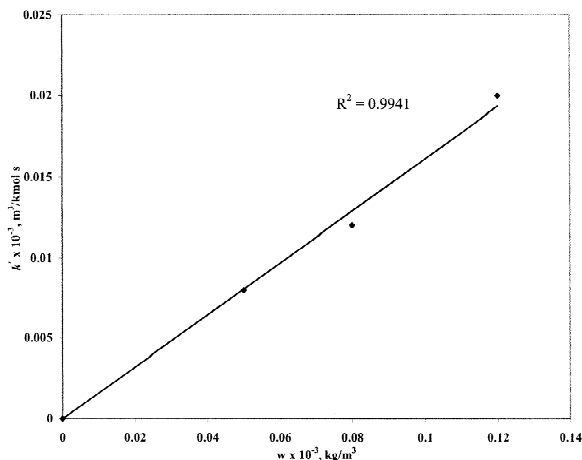

Fig. 7. Effect of mole ratio. Catalyst loading: Indion-170 = 120 kg/m³, particle size = 400–450 μm, temperature = 80 °C, speed of agitation = 13.33 rps. ♦, 1:3; ■, 1:5; ▲, 1:10; ●, 1:15.

Fig. 6. Plot of rate constant, k' v/s. catalyst loading, w. Particle size = 400–450 μm, temperature = 80 °C, speed of agitation = 13.33 rps, ethanol to maleic acid mole ratio = 5:1.

Fig. 8. Typical kinetic plot for effect of mole ratio. Particle size = 400–450 μm, temperature = 80 °C, speed of agitation = 13.33 rps, catalyst loading, Indion-170 = 120 kg/m³. ▲, 1:5; ■, 1:10; ♦, 1:15.

increased, the conversion of maleic acid also increased. Beyond 1:15 there was no significant change in conversion. The plot of L.H.S. of Eq. (28) vs. t was plotted and it was found that the data fits well (Fig. 8).
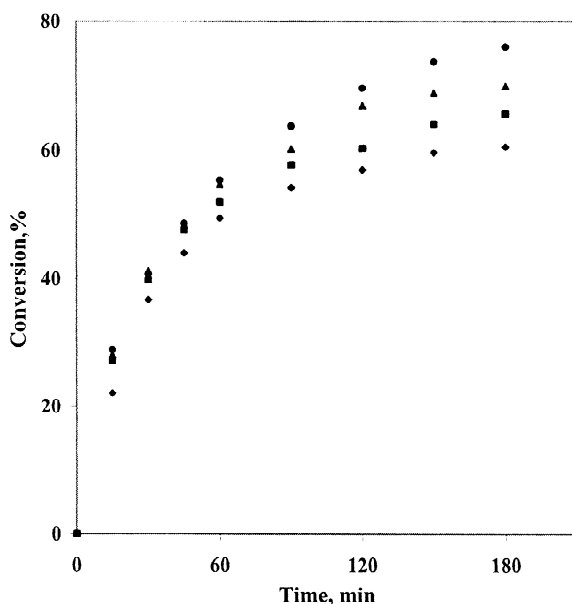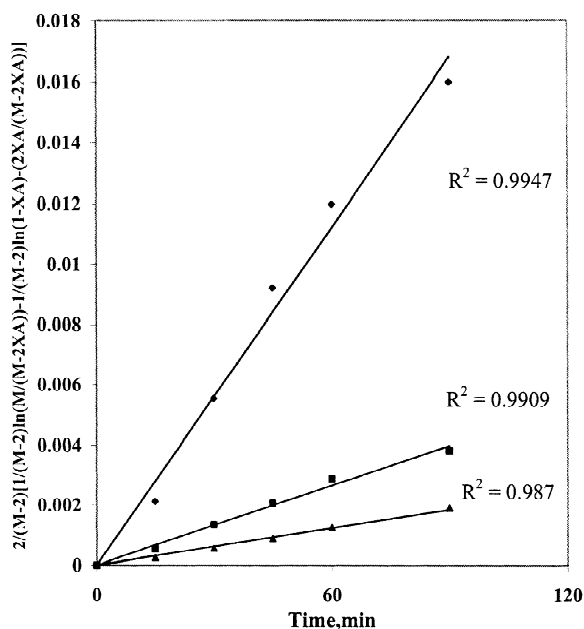
3.7. Effect of temperature

The effect of temperature on conversion under otherwise similar conditions was studied in the range of 50–80 °C, (Fig. 9). It was seen that the conversion increases with temperature, indicating absence of mass transfer effects.

It was observed that a plot of L.H.S. of Eq. (28) vs. t is a straight line passing through origin, thus suggesting that the model developed is adequate to represent the system (Fig. 10) for different temperatures. The slope of the straight line gave the value of k' from which the value of k_1 was calculated. The Arrhenius plot (Fig. 11), where $\ln k_1$ was plotted against $1/T$ to get the activation energy as 14.2×10^3 kcal/kmol, which is a typical value of kinetically controlled reactions.

3.8. Reusability studies

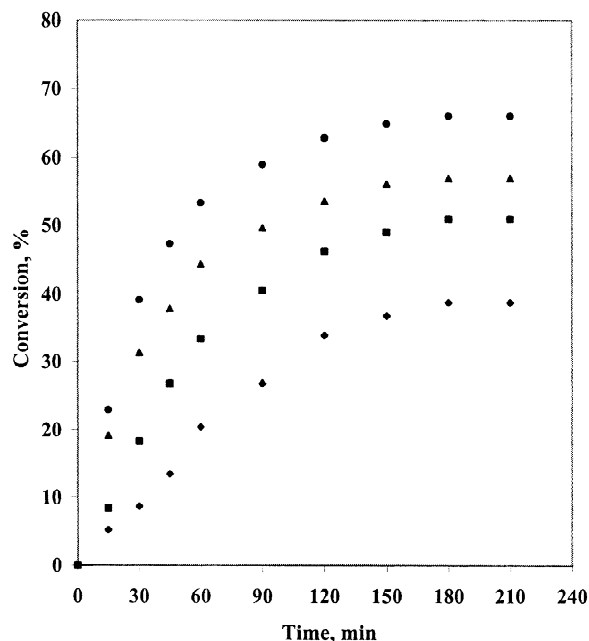The catalyst after the experiment was washed with methanol and dried at 110 °C for reuse
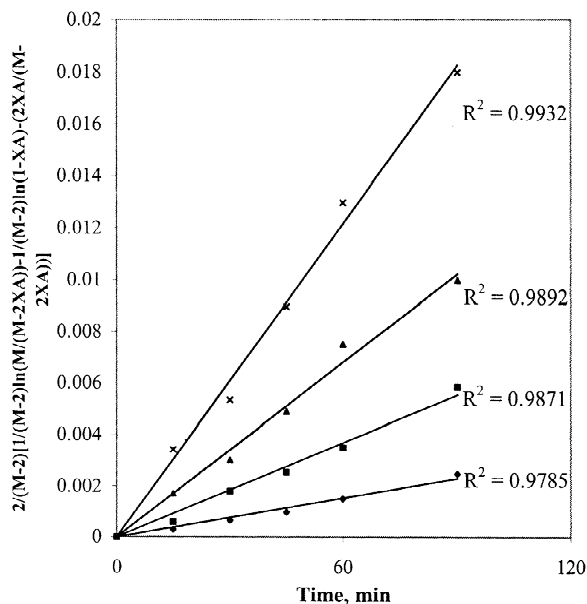
Fig. 10. Typical kinetic plots for the effect of temperature. Catalyst loading, Indion-170 = 120 kg/m³, particle size = 400–450 μm, speed of agitation = 13.33 rps, mole ratio of ethanol to maleic acid = 5:1. ♦, 50 °C; ■, 60 °C; ▲, 70 °C; ×, 80 °C.

Fig. 9. Effect of temperature. catalyst loading: Indion-170 = 120 kg/m³, particle size = 400–450 μm, speed of agitation = 13.33 rps, mole ratio of ethanol to maleic acid = 5:1. ♦, 50 °C; ■, 60 °C; ▲, 70 °C; ●, 80 °C.
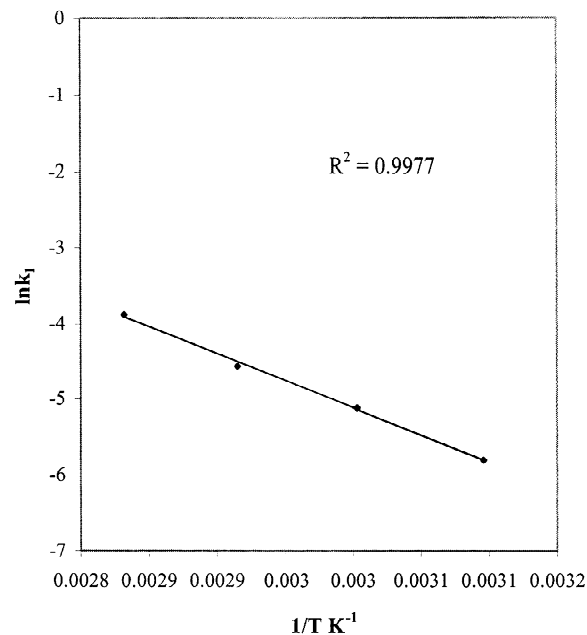
Fig. 11. Arrhenius plot of $\ln k_1$ vs. $1/T$. Catalyst loading, Indion-170 = 120 kg/m³, particle size = 400–450 μm, speed of agitation = 13.33 rps, mole ratio of ethanol to maleic acid = 5:1.

(Fig. 12). It was observed that the catalyst was reusable three times giving conversions comparable to the fresh catalyst under otherwise the
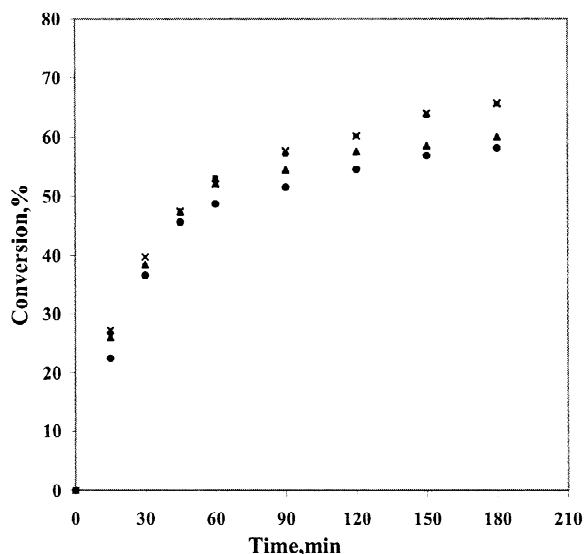
Fig. 12. Effect of reusability. Catalyst loading, Indion-170 = 120 kg/m^3, particle size = 400–450 μm, temperature = 80 °C, speed of agitation = 800 rpm, ethanol to maleic acid mole ratio = 5:1. ×, Fresh use; ■, first use; ▲, second use; ♦, third use.

same conditions. Thus there was no deactivation of the catalyst.

4. Conclusions

The esterification of maleic acid with ethanol was studied by using different solid acid catalysts, Amberlyst-36, Amberlyst-15, Abmerlyst-18, Indion-170, Filtrol-24, 20% DTP/K-10. The order of catalytic activity was found to be: Amberlyst-36 > Amberlyst-15 > Indion-170 > Amberlyst-18 > Amberlite IRA 400 > Filtrol-24 > 20% DTP/K-10. Indion-170 was used for further experiments. It was observed that the catalyst has excellent reusability. A pseudo-homogeneous kinetic model was employed to fit the experimental data and the activation energy was found to be 14.2 kcal/mol, which also suggested that this reaction was intrinsically kinetically controlled.

5. Nomenclature

ε	Fractional porosity, dimensionless
τ	Tortuosity, dimensionless
ρ_L	Liquid density, kg m^{-3}
μ_L	Viscosity of liquid, kg/m s.
ρ_p	Density of particle, kg m^{-3}
ψ	Shape factor, dimensionless
A	Reactant A, maleic acid
$[A_s]$	Concentration of A at the surface of the catalyst, kmol/m^3
$[A_0]$	Concentration of A in the bulk, kmol/m^3
a_p	Surface area per unit volume of the catalyst, m^2/m^3
B	Reactant B, ethanol
$[B_s]$	Concentration of B at the surface of the catalyst, kmol/m^3
$[B_0]$	Concentration of B in the bulk, kmol/m^3
C_A	Concentration of A, kmol/m^3
C_B	Concentration of B, kmol/m^3
C_M	Concentration of M, kmol/m^3
C_W	Concentration of W, kmol/m^3
C_E	Concentration of E, kmol/m^3
C_{Ao}	Initial concentration of A, kmol/m^3
D_{AB}	Mutual diffusion coefficient of solute A at very low concentrations in the solvent B, m^2/s
D_e	Effective diffusivity, m^2/s
D_{e-A}	Effective diffusivity of solute A, m^2/s
d_p	Diameter of the particle, m
e	Energy supplied per unit mass of slurry by agitation, m^2/s^3
k_1	Rate constant, m^3 kmol^{-1} kg^{-1} s^{-1}
K_{SL}	Solid liquid mass transfer coefficient, m/s
K_{SL-A}	Solid liquid mass transfer coefficient for species A, m/s
K_{SL-B}	Solid liquid mass transfer coefficient for species B, m/s
M	Mole ratio of C_{B0} to C_{A0}
N	Speed of agitation, rps
N_p	Power number, dimensionless
R_p	Particle radius, m
T	Absolute temperature, K
t	time, min
w	Catalyst loading, kg m^{-3}
V_L	Volume of liquid phase, m^3
X_A	Fractional conversion of A

Acknowledgements

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